

PB-247 515

SURVEY OF USERS OF THE EPA - REFERENCE METHOD FOR
MEASUREMENT OF NON-METHANE HYDROCARBONS IN AMBIENT AIR

Louis R. Reckner

Scott Environmental Technology, Incorporated
Plumsteadville, Pennsylvania

December 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

PB 247 515

Reproduced by
**NATIONAL TECHNICAL
INFORMATION SERVICE**
U.S. Department of Commerce
Springfield, VA. 22151

TECHNICAL REPORT DATA														
1. REPORT NO. EPA 650/4-75-008	2. REPORT DATE December 1974	3. REPORT TYPE PB247515												
4. TITLE AND SUBTITLE Survey of Users of the EPA - Reference Method for Measurement of Non-Methane Hydrocarbons in Ambient Air	5. REPORT DATE December 1974	6. PERFORMING ORGANIZATION CODE												
7. AUTHOR Louis R. Reckner	8. PERFORMING ORGANIZATION REPORT NO.													
9. PERFORMING ORGANIZATION NAME AND ADDRESS Scott Environmental Technology, Inc. Plumsteadville, PA 18949	10. PROGRAM ELEMENT NO. 1HA327	11. CONTRACT GRANT NO. 68-02-1206												
12. SPONSORING AGENCY NAME AND ADDRESS Office of Research and Development U.S. Environmental Protection Agency Washington, D.C. 20460	13. TYPE OF REPORT AND PERIOD COVERED	14. SPONSORING AGENCY CODE												
15. SUPPLEMENTARY NOTES														
16. ABSTRACT Scott performed a survey of users of the EPA Reference Method for measurement of non-methane hydrocarbons in ambient air which resulted in the compilation of a list of 188 NMHC analyzers operated by 70 organizations. Field evaluations were performed on instruments operated by 16 of the users. The accuracy of the NMHC data being obtained by the 16 users of the reference method was determined by presenting a series of 5 gas mixtures in high-pressure cylinders for analysis by each operator. The results for the mixture containing NMHC at a concentration close to the 0.24 ppm-C ambient air standard showed that substantial errors existed in current NMHC data. The errors are summarized below: <table border="1"> <thead> <tr> <th>Error Range</th> <th>Number of Users</th> </tr> </thead> <tbody> <tr> <td>0-10%</td> <td>1</td> </tr> <tr> <td>10-20%</td> <td>3</td> </tr> <tr> <td>20-50%</td> <td>2</td> </tr> <tr> <td>50-100%</td> <td>4</td> </tr> <tr> <td>> 100%</td> <td>6</td> </tr> </tbody> </table> An analysis of the data showed that the inaccuracies in current data make it impossible to determine whether ambient air quality is in compliance with the standard. The major factors contributing to data errors are discussed, and recommendations for improving data quality are presented.			Error Range	Number of Users	0-10%	1	10-20%	3	20-50%	2	50-100%	4	> 100%	6
Error Range	Number of Users													
0-10%	1													
10-20%	3													
20-50%	2													
50-100%	4													
> 100%	6													
17. KEY WORDS AND DOCUMENT ANALYSIS														
1. DESCRIPTORS Air Pollution Methodology Measurement	2. IDENTIFIERS OPEN ENDED TERMS Field Evaluation EPA Reference Method Non-Methane Hydrocarbon	3. COSATI Field Group 13B 7C												
18. DISTRIBUTION STATEMENT Unlimited 19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified 21. NO. OF PAGES 50 22. PRICE \$4.00														

EPA-650/4-75-008

**SURVEY OF USERS OF THE EPA -
REFERENCE METHOD
FOR MEASUREMENT
OF NON-METHANE
HYDROCARBONS
IN AMBIENT AIR**

by

Louis R. Reckner

Scott Environmental Technology
Plumsteadville, Pennsylvania 18949

Contract No. 68-02-1206

ROAP No. 26AAF

Program Element No. 1HA327

EPA Project Officer: John H. Margeson

Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, N. C. 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON, D.C. 20460

December 1974

i (a)

EPA REVIEW NOTICE

This report has been reviewed by the National Environmental Research Center - Research Triangle Park, Office of Research and Development, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into series. These broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and maximum interface in related fields. These series are:

1. ENVIRONMENTAL HEALTH EFFECTS RESEARCH
2. ENVIRONMENTAL PROTECTION TECHNOLOGY
3. ECOLOGICAL RESEARCH
4. ENVIRONMENTAL MONITORING
5. SOCIOECONOMIC ENVIRONMENTAL STUDIES
6. SCIENTIFIC AND TECHNICAL ASSESSMENT REPORTS
9. MISCELLANEOUS

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public for sale through the National Technical Information Service, Springfield, Virginia 22161.

TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 IDENTIFICATION OF USERS OF NON-METHANE HC ANALYZERS	2
3.0 PREPARATION FOR ON-SITE SURVEY	3
3.1 SELECTION OF USERS FOR ON-SITE EVALUATION	3
3.2 DEVELOPMENT OF FORMAT FOR ON-SITE SURVEY	3
3.3 UNKNOWNNS FOR ANALYSIS BY USERS	4
3.4 PRELIMINARY SURVEYS	8
4.0 RESULTS OF ON-SITE SURVEY	9
5.0 DATA ANALYSIS	13
5.1 ZERO ERROR	13
5.2 SPAN ERROR	16
5.3 INSTRUMENT RESPONSE TO HIGHER HYDROCARBONS	19
5.4 PRECISION OF METHANE AND THC DATA	19
6.0 DISCUSSION OF RESULTS	23
6.1 AREAS FOR IMPROVED TECHNIQUES	23
6.2 INSTRUMENT CAPABILITY	26
6.3 PERFORMANCE OF OTHER TYPES OF NMHC INSTRUMENTS	28
7.0 CONCLUSIONS AND RECOMMENDATIONS	29
7.1 CONCLUSIONS	29
7.2 RECOMMENDATIONS	29
 APPENDIX	
Table A-1 - Users of Non-Methane Hydrocarbon Analyzers	A-1
Figure A-1 - Non-Methane Hydrocarbon Analyzer On-Site Evaluation Format	A-6



SET 1385 06 1274

ABSTRACT

Scott Environmental Technology, Inc. performed a survey of users of the EPA Reference Method for measurement of non-methane hydrocarbons in ambient air which resulted in the compilation of a list of 188 NMHC analyzers operated by seventy organizations. Field evaluations were performed on instruments operated by sixteen of the users. The evaluations were performed in the East, Midwest and Far West and included state and local air pollution control agencies as well as private consulting firms.

The accuracy of the NMHC data being obtained by the sixteen users of the reference method was determined by presenting a series of five gas mixtures in high-pressure cylinders for analysis by each operator. The results for the mixture containing NMHC at a concentration close to the 0.24 ppm - C ambient air standard showed that substantial errors existed in current NMHC data. The errors are summarized below:

<u>Error Range</u>	<u>Number of Users</u>
0-10%	1
10-20%	3
20-50%	2
50-100%	4
> 100%	6

Detailed information regarding instrument operating conditions and operator techniques was also recorded at each user location.

An analysis of the data showed that the inaccuracies in current data make it impossible to determine whether ambient air quality is in compliance with the standard. The major factors contributing to data errors were:

1. Failure of operators to understand and/or follow the instrument manufacturers' operating instructions and the reference method procedures for NMHC as published in the Federal Register.
2. Span gases containing unknown amounts of higher hydrocarbons.
3. Span gases not in air.
4. Span gases incorrectly analyzed for methane.
5. Zero errors due to sampling system contamination and lack of adequate checkout procedures.
6. Excessive instrument zero and span drift during unattended operation.



SET 1385 06 1274

1.0 INTRODUCTION

This report covers work performed by Scott Environmental Technology, Inc. under EPA Contract No. 68-02-1206, "Survey of Users of the EPA Reference Method for Measurement of Non-Methane Hydrocarbons in Ambient Air." The program involved the identification of organizations operating non-methane hydrocarbon (NMHC) analyzers and the on-site evaluation of fifteen typical instruments. The objective was to determine the accuracy and reliability of NMHC data being recorded by users following the principles of the EPA reference method and to recommend improvements in technique which would aid in producing improved data.

An extensive survey of organizations engaged in air monitoring resulted in a compilation of 188 NMHC analyzers operated by seventy organizations. Field evaluations were performed on instruments operated by sixteen of these organizations. The evaluations were performed in the East, Midwest and Far West and included state and local air pollution control agencies as well as private consulting and testing companies. Instruments from five manufacturers were evaluated.

The accuracy of the NMHC data being obtained by the sixteen users of the reference method was determined by presenting a series of five Scott gas mixtures in high-pressure cylinders for analysis by each operator. Detailed information regarding instrument operating conditions and operator techniques was also recorded at each user location. Since the intent was to evaluate the method as being used by the operator, precautions were taken not to improve the user's technique until after all information had been recorded.

The data obtained for the test cylinders was analyzed for accuracy and precision, and the magnitude of various individual error sources was determined. Emphasis was placed on the quality of NMHC data in the area of the 0.24 ppm-C ambient air standard level. General problems with the instrumentation and techniques are discussed, and recommendations for improving the data accuracy are presented.



SET 1385 06 1274

2.0 IDENTIFICATION OF USERS OF NON-METHANE HC ANALYZERS

The first step in the program was the identification of organizations performing non-methane hydrocarbon (NMHC) analysis of ambient air according to the Reference Method for Determination of Hydrocarbons Corrected for Methane as published in the Federal Register, Vol. 36, No. 228, pp 22394-6. This method specifies the use of gas chromatographic type flame ionization hydrocarbon analyzers for the semicontinuous analysis of ambient air. It was anticipated that the several manufacturers of NMHC analyzers would cooperate in making the names of purchasers of their instruments available to Scott. However, only one company made such a list available. Other companies stated that company policy did not permit the release of purchasers' names. Appeals to high management levels to waive the policy were unsuccessful. Thus, alternate approaches were required to obtain the names of users.

The list of users was compiled through contact with organizations listed in the 1973 Directory of Governmental Air Pollution Agencies, Regional Air Pollution Control Directory, 1972 Air Pollution Consultants Guide and the Air Pollution Directory and Laboratory Guide. These publications were obtained from the Air Pollution Control Association, American Chemical Society and the EPA Project Officer. Additional contacts were made with organizations known to Scott and organizations suggested by the primary contacts.

The list of users obtained as a result of these efforts is presented in Appendix Table A-1. The location, type of organization and instrument manufacturer and model number are also included. The list contains a total of 188 instruments operated by 70 users.

The AID instrument is a portable unit designed for short term use. As such it is in a separate class from the other instruments shown, but it was included in the survey because it follows the same operating principles. Some of the other instruments have been discontinued or sold in very limited quantities.



SET 1385 06 1274

3.0 PREPARATION FOR ON-SITE SURVEY

3.1 SELECTION OF USERS FOR ON-SITE EVALUATION

The program plan called for the on-site evaluation of fifteen instruments used for monitoring ambient air by the EPA Reference Method for Determination of Hydrocarbons Corrected for Methane. The instruments were selected from the list of users given in Table A-1. The considerations in selecting the instruments were:

1. Instrument Manufacturer - At least one instrument should be chosen from each manufacturer with emphasis on those which represented the major share in use.
2. Type of Organization - The various organization types included state and local air pollution control agencies, and private consulting and testing companies.
3. Location of User - The users should be located in various areas of the United States.

The instruments evaluated in the field program are discussed in Section 4.0. Numerous revisions were made from the initial proposed list of users because certain instruments selected originally were not in operation, had been incorrectly identified by the user, or the user was not interested in participating in the program. When substitutions were necessary, every effort was made to locate a similar instrument and organization type in the geographical area.

3.2 DEVELOPMENT OF PROCEDURE FOR ON-SITE SURVEY

The primary purpose of the on-site survey was to determine whether non-methane hydrocarbon analyzers in actual use in ambient air monitoring were being operated in accordance with the EPA Reference Method, manufacturers' instructions and good laboratory practice; and to determine the accuracy of the data being collected by the users. A check list was developed to assure that the Scott chemist performing the evaluation would acquire a complete picture of the instrument operating practices and performance. A copy of this check list is included in Appendix, pages A-6 to A-11. The information areas covered in the evaluation included:



SET 1385 06 1274

1. Manufacturer's name and model number.
2. Organization category of user and use type and frequency.
3. Training and experience of instrument operator.
4. Operator's technique as compared to manufacturer's instructions, published method and good laboratory practice.
5. Instrument history including type and frequency of problems and preventive maintenance program.
6. Instrument operating conditions.
7. Calibration technique and source of calibration gases.
8. Evaluation of instrument accuracy, precision and drift.
9. User's opinion of analyzer's strong and weak points with recommendations for improvement.
10. Evaluator's opinion of analyzer's strong and weak points with recommendations for improvement.

Two additional steps were added to assure that the field survey would result in a realistic evaluation of in-use practices. First, in order to obtain frank responses from the users, each user was assured that complete anonymity would be maintained throughout the study. Appendix Table A-1, while identifying all users, maintains the anonymity of those who participated in the field survey. Secondly, so as not to bias the results the Scott chemist performing the evaluation was careful to avoid any comment or suggestion regarding any phase of instrument operation until after all evaluation data had been recorded.

3.3 UNKNOWNNS FOR ANALYSIS BY USERS

The key in the plan to determine the accuracy of data collected by the users was the presentation of several gas mixtures to the users for analysis. The composition of these mixtures would be known to Scott, but identified to the users merely as mixtures of hydrocarbons in air. The concentration data obtained by the users would then provide a measure of the accuracy of the ambient air data being collected by the users.

In order to obtain a complete picture of the users' data and to isolate specific potential sources of error, it was concluded that five test mixtures were needed. These included:



SET 1385 06 1274

1. Methane in hydrocarbon-free air to check the users' span gases.
2. Hydrocarbon-free air to check the instrument zero points.
3. Methane at a typical ambient level + higher hydrocarbons at approximately the ambient standard (0.24 ppm - Carbon).
4. Methane as in 3 + higher hydrocarbons at typically high ambient levels (~ 10 times the ambient standard).
5. Higher hydrocarbons at the same level as 4 but without methane.

The last mixture was added to explore the instrument response factor for higher hydrocarbons versus methane. It was known that flame ionization detectors generally yield a lower response to higher hydrocarbons in air than methane in air on a carbon basis. What was not known was whether the response ratio varied from instrument to instrument. This could be determined by comparing the users' data for mixture 5 (higher hydrocarbons only) to that for mixture 1 (methane only).

It was originally planned to present these mixtures to the users in push-button cans. These cans, which Scott has filled and sold over the last ten years, are readily carried in a brief case and had been shown to be stable containers for C_1 to C_6 saturates and olefins. They have proved especially useful in gas chromatographic work where a relatively small sample is required. Scott's normal procedure for preparing can mixtures is to first prepare the mixture in a high-pressure cylinder and then to fill the cans from the cylinder. Scott has developed can filling procedures which assure that the can concentrations are the same as the cylinder concentration.

A test program was carried out to determine if the can mixtures would be sufficiently stable to satisfy the needs of the field evaluation program. Three high-pressure cylinders, corresponding to mixtures 3, 4 and 5 above were prepared and a dozen cans were filled with each mixture. The cylinders and several sample cans were analyzed for methane and total hydrocarbons over a thirty-day period. The can concentrations of methane were stable throughout. The total hydrocarbons in the cans showed a small but measurable (<0.10 ppm) increase with time. It was concluded that small concentrations of higher hydrocarbons were being emitted by the can gaskets. However, it was believed that analysis of each can before and after use in the field would adequately define their THC concentration for field evaluation. The methane would be no problem.



SET 1385 06 1274

At this time Scott became aware of potential limitations in the use of the cans for checking the NMHC analyzers. EPA personnel suggested that the sample flow system used in the analyzers was different than the ordinary gas chromatograph so that sample flow rate was critical. This potential problem was investigated by testing the cans and cylinders at a nearby user location. It was found that small but significant variations occurred when successive samples were injected from the cans. The cylinder gave consistent results. The cans were then outfitted with a flow control valve and a second field evaluation was made. Consistent results were obtained for methane using a can, but the total hydrocarbon results still showed somewhat greater variation than desirable. It was also noted that the total hydrocarbon from the cans increased slightly as the can pressure decreased. The NMHC analyzers inject samples from a flowing stream, and there are restrictions downstream of the sampling loops. The flow rate thus affects the volume in the loop at the time of injection. The variations in THC results even with flow control may have been related to system contamination problems found later in the field program.

Because of the potential problems with the cans, it was decided to abandon plans for their use in favor of the high-pressure cylinders. While not nearly as convenient to transport as the cans, the cylinders were considered necessary to meet the program objectives. The same set of cylinders was used for all field evaluations.

The cylinders which had been made up with higher hydrocarbons were analyzed for individual hydrocarbons by gas chromatography. Calibration standards for the GC analysis were prepared by injecting known amounts of each C_2 to C_4 hydrocarbon into calibrated glass flasks and pressurizing the flasks to a known pressure in the vicinity of 0.5 atmosphere. This procedure is used by Scott for analyzing Cleo Tolerance Analyzed Gas Mixtures which it sells to government and industry. Methane was determined against Scott cylinder standards which are checked periodically using flask standards. Isopentane and n-hexane were calculated from the average carbon response to the C_2 to C_4 saturates.

The composition of the cylinder mixtures is given in Table 3-1. The cylinders were also analyzed for THC using a flame ionization detector (FID) continuous hydrocarbon analyzer calibrated with methane. The data show that



SET 1385 06 1274

At this time Scott became aware of potential limitations in the use of the cans for checking the NMHC analyzers. EPA personnel suggested that the sample flow system used in the analyzers was different than the ordinary gas chromatograph so that sample flow rate was critical. This potential problem was investigated by testing the cans and cylinders at a nearby user location. It was found that small but significant variations occurred when successive samples were injected from the cans. The cylinder gave consistent results. The cans were then outfitted with a flow control valve and a second field evaluation was made. Consistent results were obtained for methane using a can, but the total hydrocarbon results still showed somewhat greater variation than desirable. It was also noted that the total hydrocarbon from the cans increased slightly as the can pressure decreased. The NMHC analyzers inject samples from a flowing stream, and there are restrictions downstream of the sampling loops. The flow rate thus affects the volume in the loop at the time of injection. The variations in THC results even with flow control may have been related to system contamination problems found later in the field program.

Because of the potential problems with the cans, it was decided to abandon plans for their use in favor of the high-pressure cylinders. While not nearly as convenient to transport as the cans, the cylinders were considered necessary to meet the program objectives. The same set of cylinders was used for all field evaluations.

The cylinders which had been made up with higher hydrocarbons were analyzed for individual hydrocarbons by gas chromatography. Calibration standards for the GC analysis were prepared by injecting known amounts of each C_2 to C_4 hydrocarbon into calibrated glass flasks and pressurizing the flasks to a known pressure in the vicinity of 0.5 atmosphere. This procedure is used by Scott for analyzing Close Tolerance Analyzed Gas Mixtures which it sells to government and industry. Methane was determined against Scott cylinder standards which are checked periodically using flask standards. Isopentane and n-hexane were calculated from the average carbon response to the C_2 to C_4 saturates.

The composition of the cylinder mixtures is given in Table 3-1. The cylinders were also analyzed for THC using a flame ionization detector (FID) continuous hydrocarbon analyzer calibrated with methane. The data show that



SET 1385 06 1274

the higher hydrocarbons were ~30% lower than found by GC. This difference in response is discussed earlier in this section. The NMHC instruments in use in the field would be expected to give the same reading as the FID rather than the GC because they measure THC in air using a methane calibration standard.

TABLE 3-1 CONCENTRATIONS OF INDIVIDUAL HYDROCARBONS
IN STANDARD CYLINDERS, ppm-C

<u>Compound</u>	<u>B-1441</u>	<u>B-1442</u>	<u>B-1443</u>
Methane	1.45	1.45	0.00
Ethane	0.074	0.58	0.60
Ethylene	0.044	0.44	0.46
Propane	0.051	0.69	0.69
n-Butane	0.084	1.44	1.44
Isopentane	0.070	0.70	0.70
n-Hexane	0.024	0.24	0.24
Total HC	1.797	5.54	4.13
Total NMHC	0.347	4.09	4.13
THC Reading (FID)	1.68	4.35	2.86
NMHC*	0.23	2.90	2.86

*THC(FID) - Methane(GC)

The cylinders were analyzed for methane and THC several times prior to the field program, in the middle of the program and after its completion. All differences were within experimental error (1 to 2%), so it can be concluded that the cylinder mixtures were stable throughout the program. The important point is that the NMHC analyzers read THC by FID and the Scott FID showed no change in THC for the entire test period.



SET 1385 06 1274

3.4 PRELIMINARY SURVEYS

Two preliminary evaluations were carried out to determine the adequacy of the data format and evaluation procedures. They gave the Scott evaluator an opportunity to gain experience with the test routine and estimate the time required to complete each test.

The results of the preliminary tests showed that a significant THC response (~ 0.5 ppm-C) was obtained for the Scott zero gas. The gas had previously been analyzed against a primary standard and no hydrocarbons had been found. The zero air was checked by passing it through a heated catalyst bed and then into a FID total hydrocarbon analyzer. This reading was compared to that obtained when the catalyst bed was by-passed and found to be identical. The performance of the catalyst bed was checked by treating gas from Cylinder B-1442 (methane + higher hydrocarbons) in a similar manner. The gas read 4.35 ppm directly from the cylinder. After passage through the catalyst bed the FID gave the same reading as it did for the zero gas with and without catalyst bed exposure. This was firm evidence that the zero gas was clean, and that the readings obtained in the field were in error.



SET 1385 06 1274

4.0 RESULTS OF ON-SITE SURVEY

The field evaluation of non-methane hydrocarbon analyzers was performed from January to April, 1974. A total of sixteen users were included in the evaluation. General information regarding the sixteen users is presented in Table 4-1. The users included six in the Middle Atlantic States, five in the Midwest and five in California. Each geographical area was represented by at least one user of each type: state air pollution agency, local (city or county) air pollution agency and private company (consulting and testing laboratory). In order to maintain anonymity of the users, as discussed earlier, the numbers were assigned to the users on a random basis.

Data relating to the concentration range in use, span gas composition and concentration and gas supplier are shown in Table 4-2. The concentration data for the five Scott gas mixtures obtained by each of the users are given in Table 4-3. It should be noted that all concentrations are based on peak heights compared to the electronic zero point. This is equivalent to the manner in which the data are recorded and calculated by the data systems in use. It also represents the appearance of the recorded peaks when the instrument is operated in the normal barographic mode. During the actual tests the instruments were operated in the chromatographic mode so that the continuous output from the detector was recorded. This permitted an inspection of the data for zero shifts, peak shape, etc. which was quite useful for data interpretation.



SET 1385 06 1274

TABLE 4-1 INFORMATION ON NON-METHANE HYDROCARBON ANALYZERS EVALUATED IN USERS' FACILITIES

User No.	Instrument Mfg./Model No.	Type of User Organization	Experience of Operator (yrs)	Scott Evaluation of		Users Opinion of Instrument
				General Laboratory Condition	Operator's Technique	
1	Beckman - 6800	State	2	Excellent	Very Good	No opinion
2	Beckman - 6800	Local	2	Good	Good	Good
3	Beckman - 6800	State	-	Excellent	Good	Fair to Good
4	Beckman - 6800	State	15	Good	Very Good	No opinion
5	Bendix - 8201	Local	12	Good	Good to Very Good	Very Good
6	Beckman - 6800	Private	2	Fair	Poor to Fair	Good
7	Beckman - 6800	Local	2-1/2	Good	Good	Good
8	Beckman - 6800	Local	1/2	Good	Good to Very Good	Good
9	Beckman - 6800	Private	23	Fair	Fair to Good	Good
10	Bendix - 8201	State	24	Good	Poor to Fair	Good
11	MSA - 2472	Private	1-1/2	Good	Very Good	Fair to Good
12	AID - 514	Local	2-1/2	Good	Poor to Fair	Fair
13	Beckman - 6800	Local	10	Good	Very Good	Good
14	Beckman - 6800	Local	3-1/2	Fair	Good	Good
15	Bendix - 8200	Private	2	Fair	Poor to Fair	Poor
16	Byron - 230	Private	2	Good	Fair to Good	Good



SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

SET 1385 06 1274

TABLE 4-2 RANGE AND SPAN GAS DATA ON NON-METHANE HC ANALYZERS

User No.	Mfg./Model	Range in Use ppm	Span Gas		Gas Supplier(s)
			CH ₄ ppm	THC ppm	
1	Beckman - 6800	0-20	4.2	12.2	M&G Scientific
2	Beckman - 6800	0-20	8.5	15.4	Air Products
3	Beckman - 6800	0-20	7.5	7.5	Union Carbide
4	Beckman - 6800	0-100	44.8	51.0	Airco & Liq. Carbonic
5	Bendix - 8201	0-20	5.0	5.2	Liq. Carbonic
6	Beckman - 6800	0-100	82.5	85.0	Matheson
7	Beckman - 6800	0-20	15.3	15.3	Specialty Gas Lab.
8	Beckman - 6800	0-50	20.1	20.1	Liq. Carbonic
9	Beckman - 6800	0-7	5.2	5.2	Air Products & Scott
10	Bendix - 8201	0-10	3.0	3.0 ⁽³⁾	Linde Gas
11	MSA - 2472	0-5	2.1	2.1	Matheson & Scott
12	AID - 514	0-8	5.2	5.2	Matheson
13	Beckman - 6800	0-20	7.8	7.8	Liq. Carbonic & Air Products
14	Beckman - 6800	0-10 ⁽¹⁾	75.2	75.2	Liq. Carbonic
15	Bendix - 8200	0-20	9.4	9.4 ⁽²⁾	Matheson
16	Byron - 230	0-10	2.4	2.4	Matheson & Air Products

(1) Attenuation changed for cylinder analysis

(2) Span gas in nitrogen

(3) Span gas in argon



SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

SET 1385 06 1274

TABLE 4-3
RESPONSE OF NON-METHANE HC ANALYZERS
TO SCOTT CALIBRATION GASES

User No.	D-305			B-1394			B-1441			B-1442			B-1443		
	CH ₄ ppm	THC ppm	NMHC ppm	CH ₄ ppm	THC ppm	NMHC ppm	CH ₄ ppm	THC ppm	NMHC ppm	CH ₄ ppm	THC ppm	NMHC ppm	CH ₄ ppm	THC ppm	NMHC ppm
Scott	0.00	0.00	0.07	4.85	4.92	0.07	1.45	1.68	0.23	1.45	4.35	2.90	0.00	2.86	2.86
1	0.22	0.49	0.37	4.54	4.91	0.37	1.45	1.84	0.39	1.45	4.51	3.06	0.17	3.02	2.85
2	-0.53	0.35	0.14	4.63	4.77	0.14	0.93	1.59	0.66	0.94	4.17	2.23	-0.50	2.70	2.70
3	0.12	0.58	0.01	4.43	4.44	0.01	1.35	1.74	0.39	1.37	3.78	2.41	0.14	2.61	2.61
4	0.00	0.29	0.66	5.21	5.87	0.66	1.52	2.08	0.56	1.49	5.19	3.70	0.00	3.41	3.41
5	0.07	0.34	0.01	4.55	4.56	0.01	1.37	1.56	0.19	1.37	3.74	2.37	0.11	2.41	2.30
6	0.00	0.50	0.26	4.71	4.97	0.26	1.50	1.63	0.13	1.49	4.55	3.06	0.00	3.09	3.09
7	0.00	0.00	-0.26	5.19	4.93	-0.26	1.41	1.39	-0.02	1.28	4.37	3.09	0.00	2.90	2.90
8	0.00	0.61	0.12	4.26	4.38	0.12	1.31	1.56	0.25	1.32	3.99	2.67	0.00	2.78	2.78
9	0.30	0.84	-	-	-	-	1.57	1.84	0.27	1.58	4.65	3.07	0.27	3.34	3.07
10	0.35	0.42	4.48	4.73	9.21	4.48	1.50	3.24	1.74	1.48	7.75	6.27	0.29	5.09	4.80
11	0.06	0.10	-0.20	4.68	4.47	-0.20	1.42	1.47	0.05	1.43	4.28	2.85	0.00	2.98	2.98
12	0.00	1.36	-0.72	5.88	5.16	-0.72	1.53	2.57	1.04	1.54	4.29	2.75	0.00	3.18	3.18
13	0.11	0.24	-0.01	4.62	4.61	-0.01	1.43	1.61	0.18	1.45	4.23	2.78	0.08	2.90	2.82
14	0.00	0.10	0.05	4.38	4.43	0.05	1.30	1.46	0.16	1.31	4.10	2.79	0.00	2.66	2.66
15	-0.20	5.52	17.66	4.14	21.80	17.66	1.18	5.52	4.34	1.24	18.40	17.16	-0.23	11.30	11.30
16	-0.12	0.72	-0.51	4.65	4.14	-0.51	1.25	1.27	0.02	1.27	3.25	1.98	-0.09	2.02	2.02
Mean*	0.02	0.47	0.00	4.75	4.74	0.00	1.38	1.69	0.31	1.38	4.22	2.77	0.01	2.86	2.81
Median†	0.00	0.42	0.05	4.63	4.61	0.05	1.42	1.60	0.22	1.40	4.26	2.79	0.00	2.90	2.84

* Not including THC and NMHC for Instruments 10 and 15 which were erroneous because span gas was not in air.



SET 1385 06 1274

5.0 DATA ANALYSIS

This section presents an analysis of the data obtained by the users for the five Scott gas mixtures. Attempts are made to estimate the contribution to the overall error of individual error sources. The implications of this analysis in terms of obtaining data to meet air monitoring requirements are discussed in the following section.

The mean and median values for all of the users shown in Table 4-3 are in reasonably good agreement with the Scott values for each of the cylinders. However, the large dispersion among the data from individual users clearly indicates generally poor accuracy especially near the 0.24 ppm NMHC air quality standard. The range of errors for Cylinder B-1441, which contained 0.23 ppm NMHC, is summarized in the following table.

SUMMARY OF USER ERRORS FOR NMHC IN CYLINDER B-1441

<u>Error Range</u>	<u>Number of Users</u>
0-10%	1
10-20%	3
20-50%	2
50-100%	4
> 100%	6

Ten out of the sixteen users obtained data in error by greater than 50% of the true value and six of the ten had data in error by more than 100%. These overall errors resulted from a combination of individual error sources. Each is explored in detail in the following sub-sections.

5.1 ZERO ERROR

Zero errors for methane and total hydrocarbons are indicated by the values obtained for the Scott zero gas (Cylinder D-305). The zero error for methane can also be observed in the data for Cylinder B-1443 which contained no methane. The methane values for the zero gas recorded by the users ranged from -0.53 to 0.35 ppm. Six of the users recorded the true value of 0.00 ppm. An examination of the recorder traces showed that all of the non-zero readings were caused by baseline shifts from the automatic electronic zero as opposed to real methane peaks which have the distinctive shape characteristic of gas chromatographic peaks.

Instructions for adjusting the instrument zero are included in operating manuals. However, many of the users do not recognize the importance of checking the zero frequently, and the procedure for doing so is sufficiently complex to tax the skill of a typical operator. The methane zero error



SET 1385 06 1274

contributes an error to the NMHC value which is equal in value but with an opposite sign. Thus, even if no additional error sources were present, ten of the sixteen users would have reported NMHC data for cylinder B-1441 which was in error by greater than 20% (0.06 ppm).

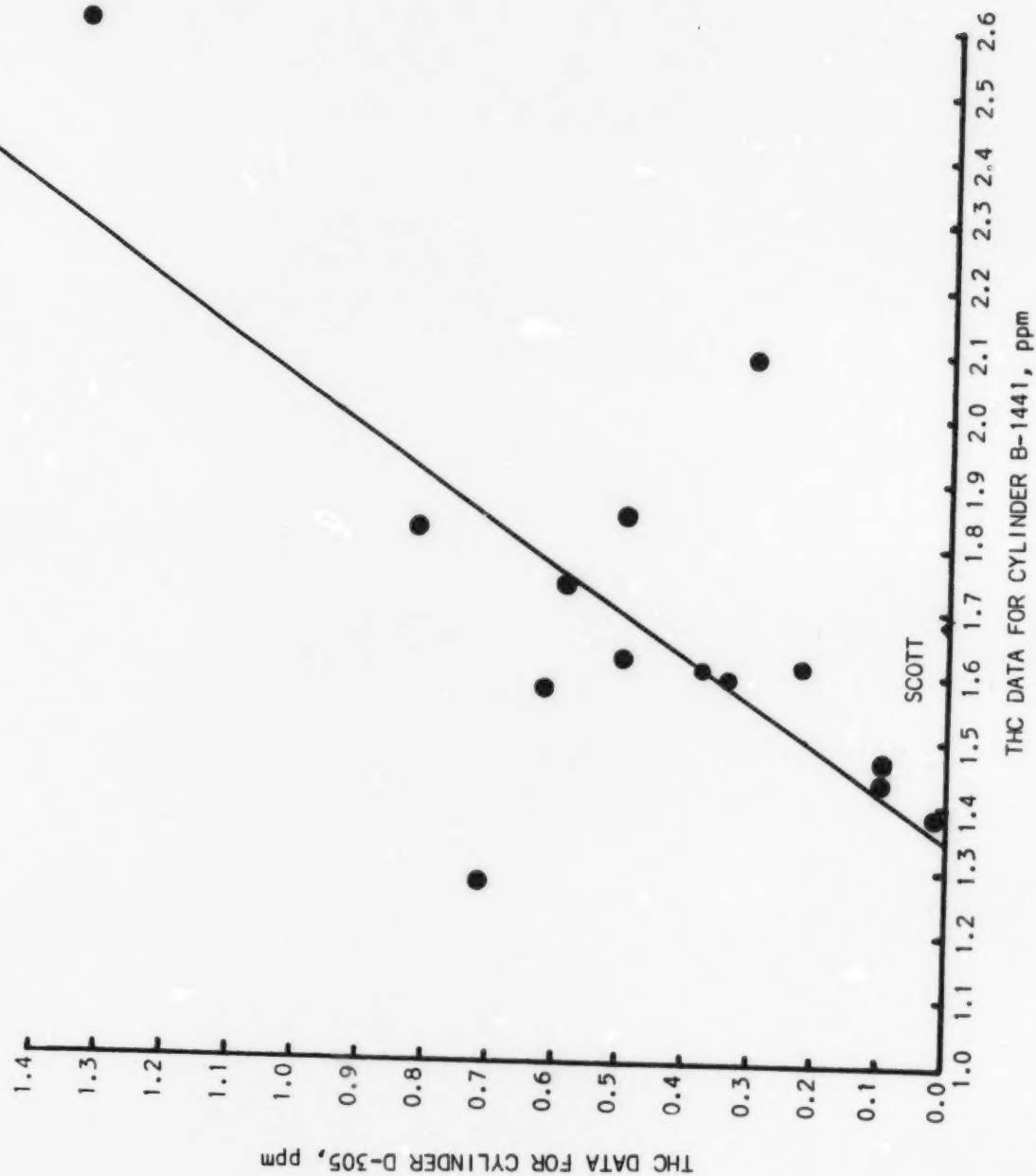
The THC values obtained for the zero gas ranged from 0.00 ppm to 5.52 ppm, and seven of the sixteen values were 0.50 ppm or greater. All of the peaks appeared to be real and not due to zero shift as was the case with the methane zero data. Since the zero gas had been demonstrated to be free of hydrocarbons as discussed in Section 3.4, and since the values obtained by the users covered a wide range it became reasonably clear that the gas was most likely being contaminated as it flowed through the analyzer. When this type of contamination occurs in a typical GC system, the level of contamination increases with the sample's residence time in the system. This was checked at User 8 where a zero gas THC reading of 0.6 ppm was found at normal sampling rates. When the zero gas flow through the sampling system was stopped one minute before injection, subsequent sample analysis showed approximately 1.2 ppm THC. When the sample flow was stopped entirely and gas in the loop was injected a THC concentration in excess of 1.5 ppm was obtained.

The THC values for Cylinder B-1441 (0.23 ppm NMHC) are plotted against the THC readings for the zero gas in Figure 5-1. Data for the two users who did not calibrate with methane in air are not included. It can be seen that there was a strong tendency for the users showing higher zero THC values to obtain higher THC values for B-1441. Errors in THC span gas values would also affect the data. This probably accounts for the outlier points for Users 4 and 16 as these two users also reported outlier values for the Scott span gas (Cylinder B-1394).

It thus appears that zero errors for both methane and THC are a major source of error in the data for Cylinder B-1441 obtained by the various users. It is our opinion that the manufacturers' claim that zero gas is not needed for this type of analyzer is not valid. They base their claim on the fact that all hydrocarbons are removed from the carrier by the catalytic purifier and the automatic zeroing systems provide a true zero point. Our data indicate that these features do not necessarily detect problems which result in erroneous zero readings and subsequent inaccurate aerometric data.



FIGURE 5-1
COMPARISON OF USER THC DATA
FOR CYLINDER B-1441 TO D-305 (ZERO GAS)



SET 1385 06 1274

5.2 SPAN ERROR

The span error for methane can be estimated from the methane data for the Scott span gas (Cylinder B-1394). First, the data must be adjusted for any CH₄ zero error due to baseline shift. Since this is a constant value, it affects the actual instrument response at the span point as well as in the analysis of B-1394. The corrected value is obtained from the following equation:

$$C_A = \frac{R_A - R_0}{C_S - R_0} \times C_S$$

where:

C_A = corrected concentration of A

R_A = read concentration of A

R_0 = read concentration of zero gas

C_S = stated concentration of span gas

Methane data for Cylinder B-1394 corrected in this manner are shown in Table 5.1. The adjusted values show that four of the fifteen users obtained results within $\pm 5\%$ of the Scott value and twelve of fifteen obtained results within $\pm 10\%$. The users values averaged several percent lower than the Scott value. Exhaustive reanalysis of Cylinder B-1394 has convinced us that the stated value is accurate to $\pm 1\%$.

It would be desirable to have a smaller error in the span gas concentrations than estimated above for fifteen users. However, even with a 10% error the effect on the NMHC data at the 0.23 ppm level would be minimal because the errors are compensated to a considerable degree in the subtraction process (THC - CH₄). Assuming that no higher hydrocarbons are present in the span gas, a 10% error at the span level would result in a 10% error in the NMHC values or 0.02 at the 0.24 ppm level. Thus, span gas CH₄ error is not a major contributor to errors in data for Cylinder B-1441.

Span errors for THC can likewise be estimated from THC data for B-1394. Despite the fact that the published reference method clearly states that the span gas shall be in air, Users 10 and 15 had span gases in argon and nitrogen, respectively. This led to gross inaccuracies at all concentration



SET 1385 06 1274

TABLE 5-1 ADJUSTED USER METHANE DATA
FOR CYLINDER B-1394

<u>User No.</u>	<u>Read CH₄ ppm</u>	<u>Adjusted CH₄ ppm</u>
Scott	4.85	4.85
1	4.54	4.57
2	4.63	4.86
3	4.43	4.39
4	5.21	5.21
5	4.55	4.55
6	4.71	4.71
7	5.19	5.19
8	4.26	4.26
10	4.73	4.97
11	4.68	4.77
12	5.88	5.88
13	4.62	4.60
14	4.38	4.38
15	4.14	4.25
16	4.65	4.55
Mean	4.75	4.73
Median	4.63	4.60



SET 1385 06 1274

levels so this data has been omitted from all data analyses. A further shortcoming in following the reference procedure was several users use of span mixtures containing significant amounts of higher hydrocarbons instead of methane alone. Finally, almost all of the users disregarded the method specification that the span gas should correspond to 80% of full scale. While some of these factors do not necessarily lead to invalid data, they showed that the majority of users were either unfamiliar with or disregarded the prescribed reference method for non-methane hydrocarbons.

It is not practical to adjust the THC values for Cylinder B-1394 for zero error because the error might well vary with concentration. An examination of the reported data shows that only three users obtained values differing from the Scott value by more than 10%. A look at the NMHC values for this mixture can be more revealing as to potential errors. It can be seen that half of the users obtained NMHC values within ± 0.1 ppm of the Scott value, but the remaining values showed very large variations from the Scott value. The negative values for five users are most likely the result of the presence of higher hydrocarbons in the span gas. In each of these cases the span gases were labeled as having identical methane and THC. Of the users obtaining high positive NMHC values, User 1 is brought into the proper range by correcting the CH_4 value for zero error, User 4's error appears to be due to an overstating of the higher hydrocarbons in the span gas and User 6's error may be due to THC zero error.

The NMHC data for Cylinder B-1394 show that substantial errors are caused by inconsistencies between the labeled CH_4 and THC concentrations of the span gas. That is, if both CH_4 and THC values are in error by the same amount, only a small error results, but if one is correct and the other in error or one value is high and the other low, very large inaccuracies occur in ambient air data. It is interesting to note that the users who obtained the best NMHC data for Cylinder B-1394 also obtained relatively accurate NMHC data for Cylinder B-1441.



SET 1385 06 1274

5.3 INSTRUMENT RESPONSE TO HIGHER HYDROCARBONS

It is known that flame ionization detectors yield a greater response to methane in air than to a like number of carbon atoms of higher hydrocarbons in air. The difference is approximately 30%, that is 1.0 ppm carbon of higher hydrocarbons gives the same response as 0.7 ppm methane. The difference can vary depending on fuel and sample flow rates, detector configuration, etc. In the user evaluation, efforts were made to determine whether this relative response varied from instrument to instrument. The various error sources discussed previously tended to mask possible response variations. The best estimate can be obtained by comparing the THC data for Cylinder B-1394 (essentially all methane) to that for Cylinder B-1443 (all higher hydrocarbons). The users THC data for these two mixtures are plotted in Figure 5-2. Other error sources caused a wide variation from user to user for each mixture, but for each user the errors should be similar for the two mixtures. If this assumption is true, then the data in Figure 5-2 should fall on a straight line unless there are variations in response. In fact the data points fall within approximately $\pm 10\%$ of the mean slope of all points. This indicates that there may well be response variations but the error should not be expected to exceed 10% of the THC value. A firmer conclusion cannot be drawn because of larger errors from other sources. The data do confirm, however, that higher hydrocarbons yield a lesser response than methane.

5.4 PRECISION OF METHANE AND THC DATA

The precision of the data from each of the users was determined from results obtained for five consecutive injections of the user's span gas. The precision was calculated according to the following equation:

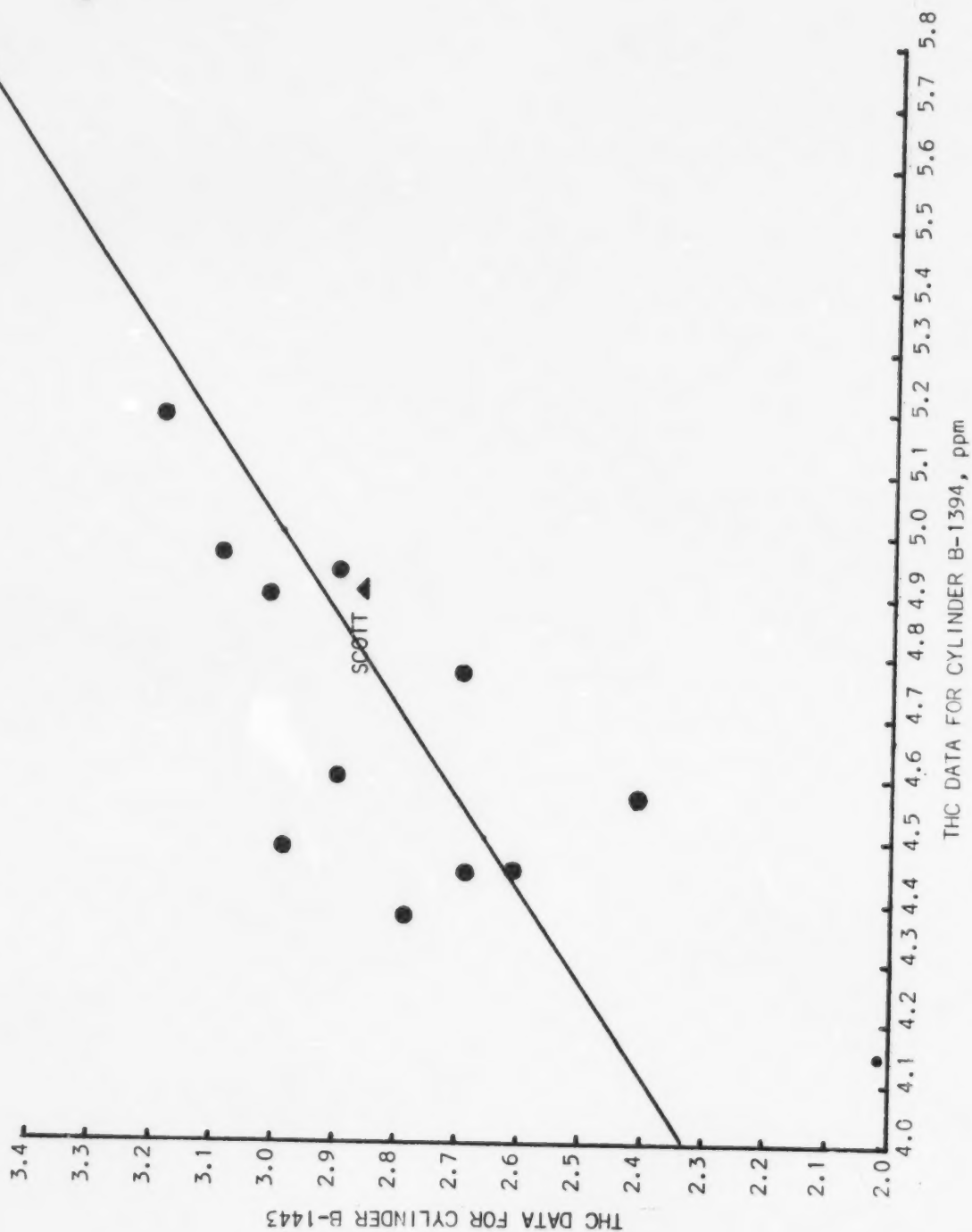
$$\text{Precision} = \text{Std. Deviation}(95\%) \ 2S = 2 \sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}}$$

Precision is expressed in ppm and thus related to the concentration of the span gas. Another user to user comparison can be obtained from the coefficient of variation which is expressed in percent. This is calculated as:

$$\text{Coefficient of Variation (CV)} = \frac{\text{Standard Deviation}(c)}{\text{Mean } (\bar{X})} \times 100$$



FIGURE 5-2
COMPARISON OF USER THC DATA
FOR CYLINDER B-1394 (METHANE) AND
CYLINDER B-1443 (HIGHER HYDROCARBONS)



SET 1385 06 1274

The precision and coefficient of variation for each instrument are presented in Table 5-5. Errors due to precision are small compared to errors discussed previously. In addition, these errors are random so they would have little effect on hourly averages. The previous errors were systematic in nature so they would have a direct effect on all data points.



SET 1385 06 1274

TABLE 5-5 PRECISION OF METHANE AND THC DATA

User No.	Methane			Total Hydrocarbons		
	Conc. ppm	Precision ppm	Coeff.of Variation %	Conc. ppm	Precision ppm	Coeff.of Variation %
1	4.2	0.34	4.0	12.2	0.15	0.6
2	8.5	0.10	0.6	15.4	0.09	0.3
3	7.5	0.11	0.7	7.5	0.18	1.2
4	44.8	0.07	0.1	51.0	0.19	0.2
5	5.0	0.04	4.3	5.2	0.25	2.4
6	82.5	2.82	1.7	85.0	2.80	1.6
7	15.3	0.53	1.7	15.3	0.31	1.0
8	20.1	0.14	0.3	20.1	0.28	0.7
9	5.2	0.07	0.7	5.2	0.16	1.5
10	3.0	0.06	1.0	3.0	0.20	3.3
11	2.1	0.13	3.2	2.1	0.12	3.0
12	5.2	0.80	7.7	5.2	0.11	1.1
13	7.8	0.10	0.6	7.8	0.10	0.6
14	75.2	0.25	0.2	75.2	0.95	0.6
15	9.4	0.05	0.3	9.4	0.14	0.7
16	2.4	0.10	2.0	2.4	0.09	1.9



SET 1385 06 1274

6.0 DISCUSSION OF RESULTS

The survey results presented in Section 4.0 and the data analysis in Section 5.0 show that approximately half of sixteen air monitoring organizations were collecting reasonably acceptable ($\pm 10\%$ accuracy) non-methane hydrocarbon data at relatively high concentration levels (~ 3 ppm). On the other hand only 30% were obtaining data accurate to $\pm 20\%$ at the ambient air standard level of 0.24 ppm. The questions which now must be addressed are:

1. What improvements in operating techniques can be made to improve accuracy especially at low concentrations?
2. What level of accuracy will be attainable with current instrumentation using these improved techniques?
3. Will this accuracy be acceptable for determining compliance with ambient air standards?

An answer to the third question is outside of the scope of the present work, but it must be kept in mind that the program was performed to provide information which will ultimately lead to an answer.

6.1 AREAS FOR IMPROVED TECHNIQUES

In considering means for improving techniques it must be borne in mind that the non-methane hydrocarbon analyzers are much more complex than other instruments operated in typical air monitoring stations and maintained by the same operators. Thus a typical operator is overwhelmed by the complexity of the instrument manual instructions. No more than two of the sixteen operators had attended training courses given by the manufacturers, and even they seemed to be unsure of how to assure accurate data and solve instrument problems. Furthermore, many operators were totally unfamiliar with the published reference method, or they were ignoring important sections of method specifications.

It is our opinion that some facets of NMHC instrument operation are above the capability level that would ordinarily be required of field operators of typical air monitoring instrumentation. In order to assure more accurate data without requiring the full time use of a high level technical person, we suggest that instrument performance tests be carried out



SET 1385 06 1274

by each operator on a regular and frequent schedule. If the operator could not correct any deficiencies shown in the performance tests, he would either summon another person in the organization with greater expertise or the manufacturer's field service representative.

Zero error was shown to be a significant source of error in NMHC data. This was believed due to both inaccuracies in the electronic zero setting and in the case of THC, contamination within the system. The error due to the zero setting can be eliminated by following the manufacturer's instructions for adjustment. However, the contamination problem may be more difficult to solve. It seems likely that this contamination results primarily from adsorption of hydrocarbons on sampling system surfaces during high concentration periods followed by desorption during low concentration periods rather than from hydrocarbons emitted directly by the system components. Some users reported that overnight flushing with clean air or nitrogen reduced this error.

Zero error can be identified by frequent performance checks with true zero THC air. If the response to zero air was not within certain limits, corrective action would be required before valid data could be reported.

Span error results primarily from span gases not in air, non-methane hydrocarbons present in span gas mixtures and methane incorrectly analyzed by the supplier. As discussed previously the error in span gas methane analysis produces a far smaller error in NMHC data than do the presence of other hydrocarbons or the incorrect oxygen content in the span gas. This error could be markedly reduced if all span gases furnished by suppliers were analyzed for both methane and THC and referenced against standards similar to those now provided by the National Bureau of Standards for propane.

Two further checks could determine whether valid data was being recorded. First, each user should have available a cylinder containing 1.5 to 2.0 ppm methane plus 0.24 ppm-C of higher hydrocarbons. We believe that the NMHC in such a mixture would be very stable over a long period of time. If the user would analyze this mixture with his instrument after



SET 1385 06 1274

performing the zero and span checks, he could determine the true accuracy for NMHC at the 0.24 ppm (ambient standard) level. If the NMHC reading was not within specified limits further corrective action would be necessary to report valid data. We believe that the mixture suggested above would be stable for an extended period of time. Obviously the supplier would have to reference each cylinder against a primary standard.

A second check would involve user participation in a cross-reference service. In this service subscribers are supplied with unknown mixtures for analysis every three months. Cylinders shipped to all subscribers are filled from a single large high-pressure container and are checked for uniformity. The results reported by the subscribers are statistically analyzed and reports of all data are sent to each subscriber. Cross-reference services have proved to be a valuable tool to organizations measuring mobile source emissions, but attempts to interest ambient NMHC instrument users in a similar service have been unsuccessful.

In analyzing the Scott gas mixtures, the users treated them in the same manner as their span gases. That is, they were introduced through the span gas inlet port at flow rates comparable to those used for the span gas. While this procedure was most desirable for detecting the errors discussed previously, it made it impossible to evaluate other potential errors such as those due to different flow rates between air sample and span gas and contamination in sample pump or external sampling line. To have investigated these factors for all users would have required excessive gas volumes and time. Therefore, this part of the study was limited to a few users where one or more Scott gases were introduced into the air sampling line. The results obtained were similar to those recorded when the gas was introduced in the normal manner. We have concluded that any errors were much smaller than those previously discussed. Any potential errors could be detected by the user through a performance test involving introduction of a gas mixture through the sampling line and a comparison to data for the same gas introduced as in the normal span procedure.



SET 1385 06 1274

In summation, we believe that the accuracy of the NMHC data currently being recorded can be greatly improved by providing the operators with simplified routine checkout procedures. These procedures would include specified performance tests which would show data accuracy and indicate whether repairs by an instrument specialist were required. Currently, most operators are confused by the complex instrument operating instructions. As a result the routine calibration and maintenance now performed by most users does little to either assure valid data or determine its accuracy.

6.2 INSTRUMENT CAPABILITY

The accuracy which should be expected from NMHC analyzers in current use when optimum user operating techniques are carried out will now be considered. In obtaining user data for the Scott cylinders, all users first spanned the instruments and performed other standard maintenance. Thus, the following discussion, which covers items such as instrument drift, involves errors separate from those identified previously.

The reference method for determination of hydrocarbons corrected for methane (Federal Register, Vol. 36, No. 228, pp 22394-6) contains suggested performance specifications for NMHC analyzers. The performance items which most affect NMHC data accuracy are zero drift and span drift. The specifications state that the zero and span drifts shall not exceed 1 percent of full scale per 24 hours. Our survey showed that instruments are typically operated on the 0-20 ppm range. Thus a 1% drift would be equivalent to 0.2 ppm. Since the zero and span drifts could be in opposite directions and could result in a net positive error for methane and a net negative error for total hydrocarbons, the NMHC data at $1.5 \text{ CH}_4 + 0.24 \text{ NMHC}$ could be in error by more than 0.4 ppm-C after 24 hours even if the instrument met the suggested standards. This is, of course, an extreme and probably unlikely case. A more realistic drift effect can be ascertained from an examination of actual user records.



SET 1385 06 1274

Various users performed span checks and other routine maintenance at varying frequencies ranging from daily to weekly. Even where daily checkouts were scheduled, none were performed over the weekend, so a three-day unattended operating period occurred. Some idea of the real effect of drift was obtained from data supplied by User 3 for daily span values. The practice was to analyze several samples of span gas and then adjust the instrument gain to produce a specified peak voltage for each component if necessary. The data shows that for the month of December 1973, the drift was as high as 0.4 ppm (2%) for one day and 0.8 ppm (4%) over three-day weekends. The methane drift was usually downward and it was greater than the THC drift which was usually upward. The net effect produced apparent NMHC values ranging from -0.3 to +1.1 ppm for the span gas which contained 7.5 ppm methane and 0.0 ppm NMHC. The average error was +0.5 ppm NMHC. The error at the ambient level being measured cannot be defined because the zero and span drifts were not checked separately. Nevertheless, it is clear that this instrument, which had been in use for approximately two months, had drift in excess of the 1%/day given in the suggested specifications. It is also clear that NMHC data collected twenty-four hours after a calibration check would be subject to substantial error in addition to the error determined using the cylinder mixtures.

The minimal operational period listed in the suggested performance specifications is three days. While the Scott field evaluation program did not include sufficient observations to define data accuracy after various intervals of unattended operation, there is considerable evidence which indicates that after twenty-four hours of unattended operation following optimum calibration procedures, confidence in the accuracy of the NMHC data would not be adequate to determine compliance with the 0.24 ppm ambient standard. That is, the error in NMHC due to twenty-four hour zero and span drift could in many cases be equal to or greater than the standard value itself.

The performance tests suggested in Section 6.1 would permit the users to determine data accuracy after various periods of unattended operation prior to instrument adjustment. While this would not improve the accuracy of prior data it would show whether or not it was valid as well as indicate the frequency of checkout required to assure a specified data accuracy.



SET 1385 06 1274

Other suggestions which would alleviate present instrument shortcomings include scheduled checkout just prior to the 6 a.m. to 9 a.m. period to which the standard applies, and automatic injection of zero and span gases at hourly intervals. This latter feature is currently available in other instruments used for aerometric and source emission measurements. In some systems automatic electronic adjustments for zero and span drift are made. In order to determine the need for these features, the degree of data accuracy required to determine compliance with the standards must first be defined. Then the capability of the various NMHC analyzers on the market for providing the required accuracy must be determined through performance tests. If available instruments do not provide sufficient accuracy, the addition of automatic zero and span gas injection systems would probably increase accuracy to the required level.

6.3 PERFORMANCE OF OTHER TYPES OF NMHC INSTRUMENTS

In a few cases users had identified instrumentation other than that of the GC type as meeting the reference method. The usual method involved the use of charcoal scrubbers to remove non-methane hydrocarbons from the air stream. Two continuous analyzers of this type were evaluated briefly in the field program. In both cases the results showed completely unsatisfactory performance. The large amount of instrument noise and drift made it impossible to determine when equilibrium to the Scott gases had been reached. The operators appeared to be aware that the instruments were obsolete and unreliable, and they were doing little to improve instrument operation.

A number of users reported that they were determining NMHC with a combination of a continuous FID analyzer for THC with a separate GC for methane on a periodic basis. None of these combinations were evaluated.



7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The information gathered in the field evaluation of non-methane hydrocarbon (NMHC) analyzers shows that ambient air NMHC data being collected by the large majority of organizations is subject to substantial errors, especially at low concentrations in the vicinity of the ambient air standard of 0.24 ppm-C. The inaccuracies in the data make it impossible to determine whether the ambient air quality is in compliance with the standard.

The major factors contributing to these errors include:

1. Failure of operators to understand and/or follow the instrument manufacturers' operating instructions and the reference method procedures for NMHC as published in the Federal Register.
2. Span gases containing unknown amounts of higher hydrocarbons.
3. Span gases not in air.
4. Span gases incorrectly analyzed for methane.
5. Zero errors due to sampling system contamination and lack of adequate checkout procedures.
6. Excessive instrument zero and span drift during unattended operation.

Despite the above shortcomings, the NMHC data from the gas chromatographic type analyzers specified in the reference method appear to be more accurate than NMHC data obtained by other types of instruments and procedures in general use. Thus, improvements in operating techniques and in performance of existing instruments would seem to be the best approach to achieving the desired data quality. At the same time the full capability of recently developed NMHC instruments should be determined, and their potential for providing the necessary data accuracy should be evaluated at an early date.

7.2 RECOMMENDATIONS

In order to improve NMHC data accuracy to an acceptable level, we offer the following recommendations:

1. Develop simplified operating procedures which can be understood and followed by operators without extensive training. The procedures should include regularly scheduled performance tests to define data accuracy and indicate when more extensive adjustments are necessary.



SET 1385 06 1274

2. Develop reference standards for methane, THC and zero air. Specify that all calibration gases be analyzed for methane and THC through comparison to the reference standards.
3. Define instrument performance required to provide data sufficiently accurate to determine compliance with ambient air standards; revise reference method to include these performance standards.
4. Evaluate capability of existing instruments to meet revised performance standards; explore improvements in any areas not meeting standards.



SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

SET 1385 06 1274

8.0 ACKNOWLEDGEMENTS

We wish to express our thanks to the Project Officer, Mr. John H. Margeson and to Dr. John B. Clements, Chief of the Methods Standardization Branch, Quality Assurance and Environmental Monitoring Laboratory for their assistance in the planning and performance of the survey of users of NMHC analyzers.

We are also deeply indebted to those sixteen users who voluntarily participated in the field evaluation. These organizations and individuals impressed us by their fine cooperation and their deep interest in the quality of their data and means for improving it. Although their names cannot be listed here because of guarantees of user anonymity, it must be recognized that without their willingness to cooperate, Scott would have been unable to perform the major portions of the program.



APPENDIX



SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

TABLE A-1 USERS OF NON-METHANE HYDROCARBON ANALYZERS
FOR AMBIENT MONITORING
(Gas Chromatographic Type per E.P.A. Reference Method)

Name	Location	Type of Instrument /Model No.						
		Beckman 6800	Bendix 8200	Bendix 8201	Byron 200	Union Carbide 3020	MSA	AID
<u>Alabama</u>								
Mobile County Board of Health	Mobile	2						
Jefferson County Board of Health	Birmingham	3	2				4	
Huntsville Air Pollution Control Dept.	Huntsville	1						
Alabama Dept. of Public Health	Montgomery	3						
<u>Arizona</u>								
Phelps Dodge Corp.	Phoenix	1						
Arizona Div.of Air Pollution Control	Phoenix						4	
<u>California</u>								
Calif.State Air Resource Board	Sacramento	5						
Calif.Div. of Highways	Sacramento	2						
San Diego APCD	San Diego	3						
Orange Co. APCD	Anaheim	1						
Ventura Co. APCD	Ventura	1						
Environmental Systems Laboratory	Sunnyvale	1						
Bay Area APCD	SanFrancisco	13		1				
Univ. of Calif.	Riverside				1			
Datronics Systems Corporation	Panorama City	1		1				
Kern Co. APCD	Bakersfield	3						
Metronics Associates Inc.	Palo Alto			1				
Santa Barbara APCD	Santa Barbara	1						



TABLE A-1 USERS OF NON-METHANE HYDROCARBON ANALYZERS
FOR AMBIENT MONITORING
(Gas Chromatographic Type per E.P.A. Reference Method)
(contd)

Name	Location	Type of Instrument / Model No.						
		Beckman 6800	Bendix 8200	Bendix 8201	Byron 200	Union Carbide 3020	MSA	AID
Materials & Research Lab.	Sacramento	8		2				
	<u>Colorado</u>							
Nat'l Ctr for Atmospheric Res.	Boulder	1						
	<u>Connecticut</u>							
Air Compliance Dept. of Environmental Protection	Hartford			1			1	
	<u>Florida</u>							
Florida Dept. of Pollution Control	Tallahassee	5						
Hillsborough Co. Poll. Cont. Comm.	Tampa	1						
Palm Beach Co. Health Dept.	Riviera Bea.						1	
	<u>Hawaii</u>							
Hawaii State Dept. of Health	Honolulu				1			
	<u>Illinois</u>							
Air Resources Inc.	Palatine	2						
Illinois Div. of Air Poll. Cont.	Springfield		1					
NALCO Chemical Corp.	Chicago		1					
Industrial Bio- Test Labs.	Northbrook				1			
Chicago Dept. of Environmental Cont.	Chicago	1						



SET 1385 06 1274

TABLE A-1 USERS OF NON-METHANE HYDROCARBON ANALYZERS
FOR AMBIENT MONITORING
(Gas Chromatographic Type per E.P.A. Reference Method)
(contd)

Name	Location	Type of Instrument/Model No.						
		Beckman 6800	Bendix 8200	Bendix 8201	Byron 200	Union Carbide 3020	MSA	AID
	<u>Indiana</u>							
Evansville Air Pollution Control Department	Evansville						1	
	<u>Iowa</u>							
State Dept. of Health	Des Moines		1					
Linn Co. Dept. of Health	Cedar Rapids					1		
	<u>Maryland</u>							
NUS Corp.	Rockville							1
Balt. Co. Dept. of Health	Towson	4						
Geomet Inc.	Rockville				3			
Green Assoc. Inc.	Towson				1			
	<u>Massachusetts</u>							
Environmental Research & Tech.	Cambridge	6						
	<u>Michigan</u>							
GM Tech. Ctr.	Warren	1			1			
	<u>Mississippi</u>							
Mississippi Air & Water Pollution Control Commission	Jackson	1						
	<u>Missouri</u>							
Midwest Res. Inst.	Kansas City	1		1			1	1
Missouri Air Conservation Comm.	Jefferson City	8	2					
St. Louis Co. Health Dept.	Clayton							1
Monsanto Enviro-Chem. Systems Inc.	St. Louis							1
Kansas City Air Poll. Cont. Div.	Kansas City	8	2					



SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

SET 1385 06 1274

TABLE A-1 USERS OF NON-METHANE HYDROCARBON ANALYZERS
FOR AMBIENT MONITORING
(Gas Chromatographic Type per E.P.A. Reference Method)
(contd)

Name	Location	Type of Instrument /Model No.						
		Beckman 6800	Bendix 8200	Bendix 8201	Byron 200	Union Carbide 3020	MSA	AID
	<u>North Carolina</u>							
Environmental Testing Inc.	Charlotte	1						
Univ. of NC	Chapel Hill				1			
	<u>New Jersey</u>							
NJ Bur. of Air Pollution Cont.	Trenton	1						
Exxon Res. & Eng.	Linden	1						
Foster D. Snell, Inc.	Florham Park				1			
	<u>New York</u>							
NY State Dept. of Environmental Conservation	Albany	6						
Erie Co. Dept. of Health	Buffalo	1						
Nassau Co. Health Dept.	Minneola	1					1	
	<u>Ohio</u>							
Union Carbide	Cleveland				1			
Herron Testing Labs., Inc.	Cleveland							1
General Elec. Co.	Cleveland							1
	<u>Oregon</u>							
Oregon Dept. of Environmental Quality	Portland	1						



SET 1385 06 1274

TABLE A-1 USERS OF NON-METHANE HYDROCARBON ANALYZERS
FOR AMBIENT MONITORING
(Gas Chromatographic Type per E.P.A. Reference Method)
(contd)

Name	Location	Type of Instrument /Model No.						
		Beckman 6800	Bendix 8200	Bendix 8201	Byron 200	Union Carbide 3020	MSA	AID
<u>Pennsylvania</u>								
Phila.Dept. of Public Health	Philadelphia	1						
Betz Environmental Engineering	Plymouth Meeting	1						
General Elec.Co.	Valley Forge						17	
Environmental Sciences Inc.	Pittsburgh						1	
<u>South Carolina</u>								
Charleston County Health Dept.	Charleston	4						
<u>Texas</u>								
Texas Air Poll. Cont. Service	Austin	5		9				
City of Dallas Health Dept.	Dallas			1				
<u>Utah</u>								
Univ.of Salt Lake City	Salt Lake City					1		
<u>Virginia</u>								
Richmond Research Labs.	Richmond		1		1			
<u>Washington</u>								
Wash.State Univ.	Pullman	1						1
<u>West Virginia</u>								
Union Carbide Co.	S.Charleston				1			
W.Va.Air Poll. Control Comm.	Charleston				1			
<u>Wisconsin</u>								
Wisc.Dept. of Natural Res.	Madison	4						
Total		109	8	18	14	2	31	6



FIGURE A-1 NON-METHANE HYDROCARBON ANALYZER
ON-SITE EVALUATION CHECK LIST

Laboratory Name: _____ Code #: _____ Director's Name: _____
Address: _____ Operators' Name: _____

Telephone: _____

1.0 Non-Methane Hydrocarbon Analyzer

- 1.1 Manufacturer: _____ Mfg. No.: _____
- 1.2 Model No.: _____ Date of Purchase: _____
- 1.3 Type of organization using this instrument: Federal agency _____,
State agency _____, Local air pollution agency _____, University _____,
Private Contractor _____, Other _____. If other, explain: _____
- 1.4 Frequency and type of use: _____
- 1.5 Training level of operator: Education: _____
Experience: _____
- 1.6 Extent to which the operator follows the recommendations of the
instrument manufacturer and good laboratory procedure in his work:

- 1.7 General Laboratory Condition: _____

- 1.8 Other instruments used in the laboratory for air monitoring: _____



SET 1385 06 1274

2.0 Performance of Instrument

2.1 Frequency and nature of breakdowns: _____

_____.2.2 Parts repaired or replaced: _____

_____.2.3 Serviced by: Laboratory personnel _____, and/or Manufacturer's
representative _____.2.4 Preventive maintenance program consists of: _____

_____.

2.5 Estimated service maintenance costs: _____.

3.0 Instrument Operation

3.1 Physical condition of the instrument: _____

_____.3.2 Type of carrier gas (N_2 , H_2 , He, or Air) _____ cc/min.

3.3 General Operating Conditions:

Combustion gas: Oxygen (), Air (). Rate: _____ cc/min.

Fuel type: _____ Rate: _____ cc/min Temp. _____

Frequency of sampling: _____ Sample size: _____

Frequency of calibration: _____.

Operating cycle: _____
_____.

Calibration gas used: _____ Range used: _____

Zero gas used: _____.

Calibration technique: _____

_____.

Sample flow rate on bypass: _____

Sampling Rate: _____.



SLT 1385 06 1274

3.4 Type of regulator: _____.

Name: _____.

Vendor: _____.

3.5 Gas vendor: _____.

3.6 Please attach a calibration curve with data points.

3.7 Instrument Checks: _____.

3.7.1 Check user's instrument accuracy at ambient levels equivalent to standard and ambient levels typically found in urban areas. Methane at typical ambient level + C₂ to C₆ saturates and ethylene at approximately 0.24 ppm-C: _____

Results: _____

Comments: _____

3.7.2 Check methane at typical ambient level + C₂ to C₆ saturates and ethylene at approximately 2.4 ppm-C: _____

Results: _____

Comments: _____

3.7.3 Relative response of user's instruments to higher hydrocarbons versus methane using C₂ - C₆ saturates and ethylene at approximately 2.4 ppm-C: _____

Results: _____



SET 1385 06 1274

Comments: _____

- 3.7.4 Initial check of user's zero gas for contamination with both methane and other hydrocarbons using Scott's hydrocarbon-free air: _____

Results: _____

Comments: _____

- 3.7.5 Check user's span gas using methane in hydrocarbon-free air, at instrument span inlet and sample inlet.

Results: _____

Comments: _____

- 3.7.6 The precision will be determined using the user's span gas to get a degree of agreement between repeated measurements of the same concentration. This will be expressed as the average standard deviation of the single results from the mean using an average of five injections.

Results: _____



SET 1385 06 1274

Comments: _____

- 3.7.7 The linearity of the recorder will be measured by using a single source to drive the recorder in equal millivolt increments from zero input to full scale response.

Results: _____

Comments: _____

- 3.7.8 Noise determination will be obtained by operating the instrument at attenuation settings normally used for ambient monitoring. Noise will be expressed as percent of full scale. It will also be noted if the instrument is used in a lower special analysis range.

Results: _____

Comments: _____

- 3.7.9 Zero drift determination will be the changes noted in instrument output over a 16-hour period (overnight) of unadjusted continuous operation. Zero drift will be expressed in percent of full scale.

Results: _____

Comments: _____



SET 1385 06 1274

4.0 Lab opinion of the analyzer:

4.1 Strong points: _____

_____4.2 Weak points: _____

_____4.3 What would the laboratory personnel like to see changed or improved
on their analyzer? _____

5.0 Evaluator's opinion of the analyzer:

5.1 Strong points: _____

_____5.2 Weak points: _____

_____5.3 How could the system be changed or improved to give better
results? _____

NOTE: The anonymity of the reporting laboratory shall be maintained throughout
this study.

